The effect of carboxylate and *N,N'*-ditopic ligand lengths on the structures of copper and zinc coordination polymers

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Abstract

A series of one-dimensional coordination polymers with parallel chains has been prepared by linking together $M_2(O_2CR)_4$ paddle wheel units, where M is Cu or Zn and R is biphenyl or iodobenzoate, with pyrazine (pyz), 2-aminopyrazine (apyz) or 1,4-diazabicyclo[2.2.2]octane (dabco) bridging ligands. The longer length of the substituent in biphenyl-4-carboxylate (bpc) allows for greater separation of the chains in $[Cu_2(bpc)_4(pyz)]\cdot 3.8BzOH$ **1** than has been previously observed in related benzoate compounds, leading to the formation of larger channels within the structure. In $[Cu_2(bpc)_4(dabco)]\cdot BzOH$ **2** and $[Zn_2(bpc)_4(dabco)]\cdot 2DMF$ **3**, neighbouring chains are offset relative to each other, enabling them to pack more efficiently and reducing the channel width from that seen in **1**. For the 4-iodobenzoate (ibz) compounds $[Cu_2(ibz)_4(pyz)]$ **4**, $[Cu_2(ibz)_4(apyz)]\cdot 2BzOH$ **5** and $[Zn_2(ibz)_4(dabco)]\cdot 3.25DMF$ **6**, the chains are closer together than in the bpc compounds, and again when the neighbouring chains are offset with respect to each other, they are able to pack more efficiently. When similar reactions were carried out using 4,4'-bipyridyl (4,4'-bipy) as the bridging ligand, the products were very different. $[Cu(bpc)_2(4,4'\text{-bipy})(BzOH)_2]\cdot 2BzOH$ **7**, $[Zn(bpc)_2(4,4'\text{-bipy})]$ **8** and $[Zn(ibz)_2(4,4'\text{-bipy})]$ **9** all have structures in which single metal centres, as opposed to $M_2(O_2CR)_4$ dimers, are bridged into chains by the ditopic linker ligand, and the chains pack efficiently without forming channels.

Introduction

Over the past 20 years there has been growing interest in the synthesis and properties of coordination network structures.[1-5] In these materials, often referred to as metal-organic frameworks (MOFs), metal centres or aggregates are linked into extended structures by bridging organic ligands such as polycarboxylates. The interest in this area largely relates to the porous nature of many of these materials, and the permanent porosity has been explored for a wide range of applications including hydrogen storage,[6] carbon capture,[7] catalysis[8] and drug delivery.[9]

One of the key concepts in the design of these extended structures is that of the secondary building unit (SBU).[10] This is the 'inorganic' part of the network structures, and in polycarboxylate-containing materials it is typically a metal-carboxylate aggregate in which the number and orientation of the carboxylate groups is a major factor in defining the type of network adopted. One of the most common SBUs is the $M_2(O_2CR)_4$ 'paddle-wheel' dimer (Fig. 1),[11] which acts as a square planar node when the axial sites are empty or coordinated to terminal ligands. This SBU has been observed with many different metal centres, with M–M bond orders ranging from 0 to 4. The paddle wheel SBUs can be linked into two-dimensional networks using dicarboxylates,[12] and three-dimensional networks using tricarboxylates.[13]

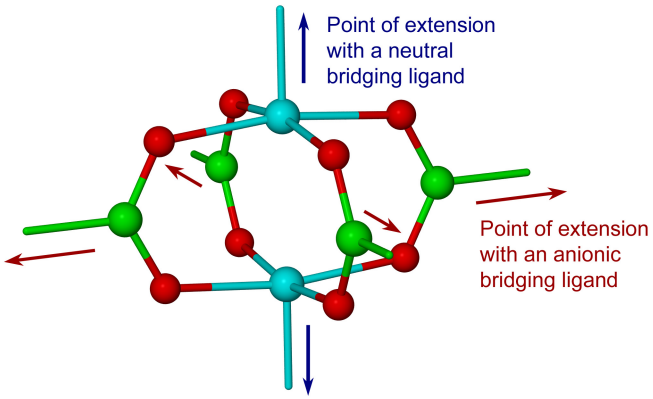

Fig. 1 The $M_2(O_2CR)_4$ 'paddle-wheel' dimer, showing points of extension into network structures.

The $M_2(O_2CR)_4$ paddle wheel SBUs can also be linked into networks through coordination of bridging ligands into the axial positions. In this way, two-dimensional metal-dicarboxylate networks have been connected into three-dimensional structures,[14] whereas discrete paddle

wheels, in which RCO_2^- is a monocarboxylate, have been linked into one- or two-dimensional networks.[15]

While the focus on porous materials has led to three-dimensional networks receiving most attention, network structures that propagate in only one or two dimensions can also exhibit interesting inclusion properties. With respect to one-dimensional polymeric systems, Takamizawa and co-workers have demonstrated that copper and rhodium monocarboxylate paddle wheels can be linked by *N*,*N*′-ditopic ligands such as pyrazine (pyz) into chains.[16] These materials adsorb guest molecules, including gases, with these guests residing in channels that are formed by imperfect packing of the chains. Thus, for example, an inclusion compound containing $[Cu_2(O_2CPh)_4(pyz)]$ and carbon dioxide has been crystallographically characterised,[17, 18] whereas the rhodium analogue has also been characterised with oxygen[19, 20] and N_2O[21] in the channels.

We reasoned that it ought to be possible to increase the size of the channels formed between the chains of one-dimensional coordination polymers containing paddle wheels by employing carboxylates with longer substituents than benzoate. In order to assess whether this is the case, we have investigated the synthesis and crystal structures of zinc and copper coordination polymers incorporating the ligands biphenyl-4-carboxylate (bpc) and 4-iodobenzoate (ibz) with a range of *N*,*N*′-ditopic ligands. Neither of these carboxylates has previously been used in the formation of coordination polymers. In fact, there has only been one previous observation of metal-carboxylate paddle wheels containing bpc, namely Cotton and Silva's report of the discrete molybdenum dimers $[Mo_2(bpc)_4]\cdot THF$ and $[Mo_2(bpc)_4(py)_2]$.[22] There have been no previous reports of metal-carboxylate dimers containing ibz.

Results and Discussion

*Structures of the biphenyl-4-carboxylate coordination polymers $[Cu_2(bpc)_4(pyz)]\cdot 3.8BzOH$ **1**, $[Cu_2(bpc)_4(dabco)]\cdot BzOH$ **2** and $[Zn_2(bpc)_4(dabco)]\cdot 2DMF$ **3***

The asymmetric unit for **1** consists of one copper atom, two bpc ligands and half a pyrazine molecule. Within the asymmetric unit there is 90 % of a benzyl alcohol molecule which was located crystallographically; the oxygen atom of this was equally disordered over two positions. There was also some highly disordered solvent which approximated to one

molecule of benzyl alcohol per asymmetric unit. Through a space group inversion centre, the structure extends into copper paddle wheel dimers, which are linked by the pyrazine ligands into one-dimensional chains (Fig. 2a).

Compounds **2** and **3** form isostructural materials, their asymmetric units each consisting of two half-occupancy metal centres, two bpc ligands and one half-occupancy dabco ligand. For **2**, a fragment of highly disordered solvent was also present, which equated to half a benzyl alcohol per asymmetric unit. In **3**, there was an ordered DMF molecule located within the channels. In a similar manner to **1**, metal paddle wheel dimers are formed, which are linked into chains by the dabco ligands (Fig. 2b,c).

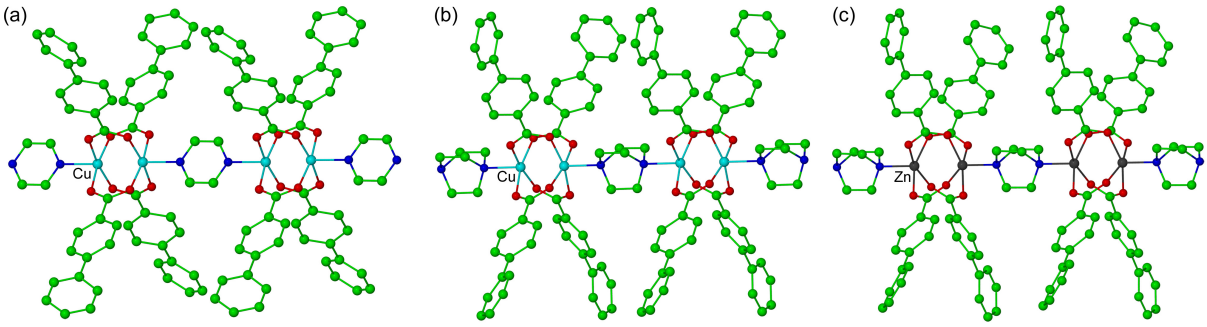

Fig. 2 Parts of the coordination polymer chains present in the crystal structures of (a) $[Cu_2(bpc)_4(pyz)]\cdot 3.8BzOH$ **1**, (b) $[Cu_2(bpc)_4(dabco)]\cdot BzOH$ **2** and (c) $[Zn_2(bpc)_4(dabco)]\cdot 2DMF$ **3**. Hydrogen atoms have been omitted for clarity.

In **1-3**, the one-dimensional chains pack parallel to each other, generating channels of approximate dimensions 10.4 × 5.7 Å for **1**, 6.2 × 2.1 Å for **2** and 6.0 × 1.8 Å for **3**, as shown in Fig. 3 (dimensions quoted are from edge-of-atom to edge-of-atom, taking into account the van der Waals radii). The difference in channel sizes reflects the difference in packing of the chains, which is in turn dictated by the ligand conformations and the relative positions of the paddle wheels on neighbouring chains. In **1**, there is a small twist between the phenyl rings in the bpc ligands (27° and 33°), and the chains pack with the biphenyl groups close to each other, supported by C–H···π interactions between aromatic rings. This leaves a relatively wide channel (Fig. 3a) in which the included benzyl alcohol molecules are accommodated. The distance between chains is 13.4 Å along the *b* axis, with neighbours maximally offset, such that a copper paddle wheel dimer on one chain is adjacent to a pyrazine on a neighbouring chain. The distance between chains is longer – 16.5 Å – along the *c* axis, and in

this case the chains are arranged with the paddle wheels on one chain adjacent to those on the neighbour.

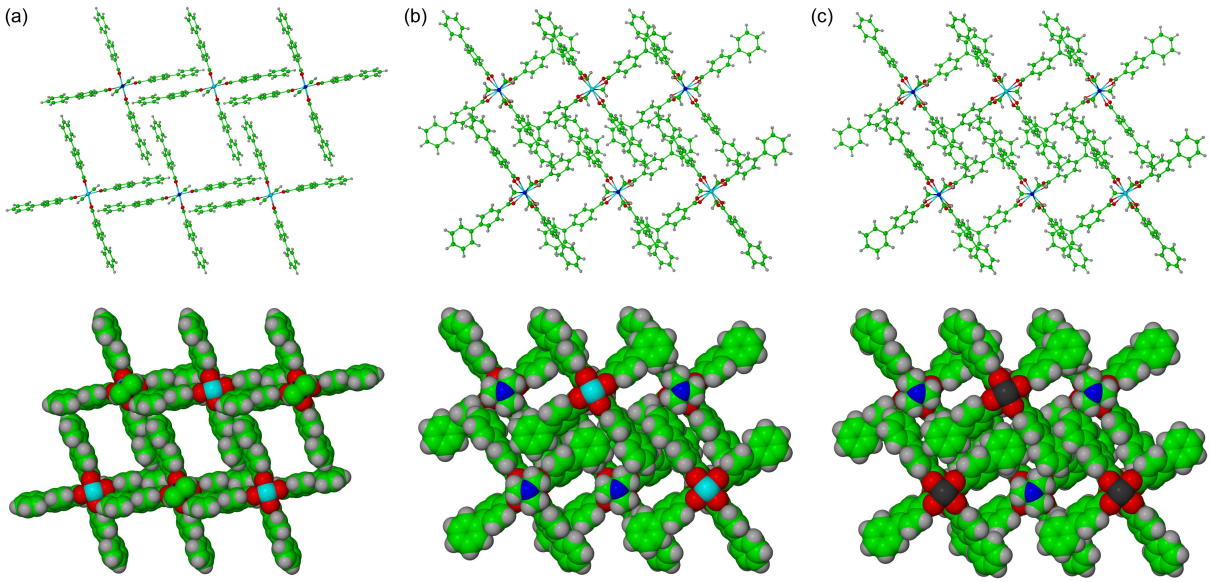

Fig. 3 Packing of the chains in the crystal structures of (a) $[Cu_2(bpc)_4(pyz)]\cdot 3.8BzOH$ **1**, (b) $[Cu_2(bpc)_4(dabco)]\cdot BzOH$ **2** and (c) $[Zn_2(bpc)_4(dabco)]\cdot 2DMF$ **3**. Included solvent molecules have been removed for clarity.

In **2** and **3**, the twists between the phenyl rings in the bpc ligands are greater than those in **1** (50° and 27° for **2**, 45° and 31°/26° for **3**), with one notably large torsion evident in both structures. The skewing of the $M_2(O_2CR)_4$ dimer (O···M···M···O torsion angles 16° - 21°, *cf.* 1° for **1**), coupled with twisting of the phenyl ring relative to the carboxylate group, ensures that some of the phenyl rings lie almost perpendicular to the channel directions, hence reducing their widths. This twisting of the ligands allows them to interdigitate with those on neighbouring chains, and this is supported by C–H···π interactions. The net effect is a decrease in the distance between chains (11.7 Å, 13.3 Å for **2**, 11.5 Å, 13.4 Å for **3**) with respect to those in **1**, and a consequent reduction in channel width as shown in Fig. 3b,c.

X-ray powder diffraction showed that bulk samples of **1** were phase impure, limiting activation studies to single crystals. Attempts to remove the benzyl alcohol from **1** by placing these single crystals under vacuum led to degradation and loss of crystallinity. Thermogravimetric analysis on **2** showed a 9.0 - 9.5 % mass loss up to 160 °C which can be attributed to the loss of the benzyl alcohol (calc. 9.5 %). However, crystals of **2** degraded in air, with cracks observed after a few hours. Thermogravimetric analysis on **3** gave an initial

13 % mass loss up to 170 °C, consistent with the loss of DMF (calc. 12.4 %), though powder diffraction data showed that solvent loss was accompanied by loss of crystallinity.

Structures of the 4-iodobenzoate coordination polymers $[Cu_2(ibz)_4(pyz)]$ ***4****, $[Cu_2(ibz)_4(apyz)]\cdot 2BzOH$* ***5*** *and $[Zn_2(ibz)_4(dabco)]\cdot 3.25DMF$* ***6***

The asymmetric unit for **4** consists of two half-occupancy copper centres, half a pyrazine molecule and two 4-iodobenzoate ligands. The phenyl ring of the 4-iodobenzoate ligand containing I(2) is positionally disordered in a 65:35 ratio. The copper centres and 4-iodobenzoate ligands form copper paddle wheels, and these are connected by the pyrazine ligands into one-dimensional chains (Fig. 4a).

Compound **5** forms similar paddle wheel moieties to those in **4** although the asymmetric unit is different, consisting of two copper centres bridged by four coordinated 4-iodobenzoate ligands, and a coordinated 2-aminopyrazine linker. The amino group is disordered over three sites in a 50:25:25 ratio. There was also an area of diffuse solvent, included as two molecules of benzyl alcohol per asymmetric unit. The 2-aminopyrazine linker in **5** plays the same role as the pyrazine ligand in **4**, connecting the paddle wheels into chains (Fig. 4b).

The asymmetric unit for **6** consists of four independent zinc atoms, eight 4-iodobenzoate ligands, two dabco ligands and six and a half included DMF molecules. One of the dabco ligands is disordered in 60:40 ratio. Two of the zinc centres and four of the 4-iodobenzoates make up a complete paddle wheel moiety, with the other two zinc centres forming two halves of paddle wheel units, each with two 4-iodobenzoates. The dabco ligands connect these paddle wheels into chains (Fig. 4c).

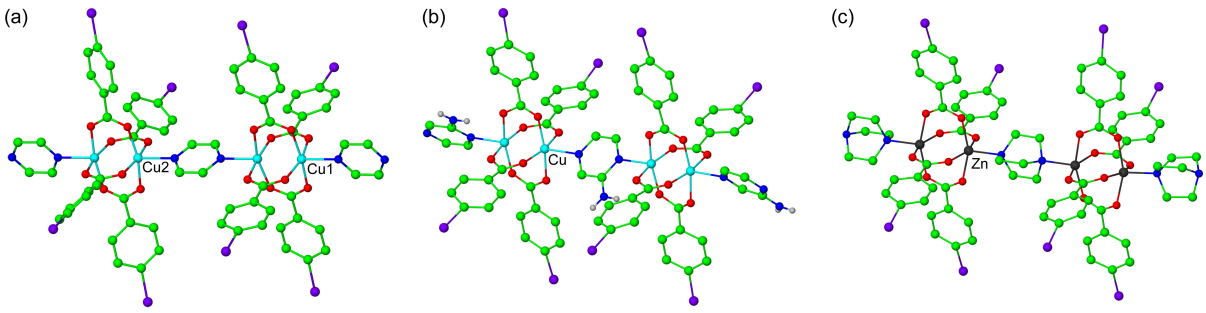

Fig. 4 Parts of the coordination polymer chains present in the crystal structures of (a) $[Cu_2(ibz)_4(pyz)]$ **4**, (b) $[Cu_2(ibz)_4(apyz)]\cdot 2BzOH$ **5** and (c) $[Zn_2(ibz)_4(dabco)]\cdot 3.25DMF$ **6**.

The chains in compounds **4-6** all lie parallel to each other, in a similar manner to those in **1-3**. For **4** (Fig. 5a) the chains are linear, with adjacent pyrazine ligands in each chain almost perpendicular to each other, while adjacent paddle wheel dimer units are slightly offset. For the paddle wheels containing Cu(1), the phenyl rings are virtually co-planar with the carboxylate groups (angle between mean planes 4°), whereas for those containing Cu(2) there is a significant twist between the comparative planes (37°). The distance between neighbouring chains is approximately 9.4 Å along both *a* and *b* axes and, as shown in Fig. 5a, there are no accessible channels. There is a degree of interdigitation, which places the iodine atoms from one chain proximate to the pyrazine rings of the neighbouring chain. This interdigitation lowers the distance between the chains, and hence reduces the percentage void space within the structure.

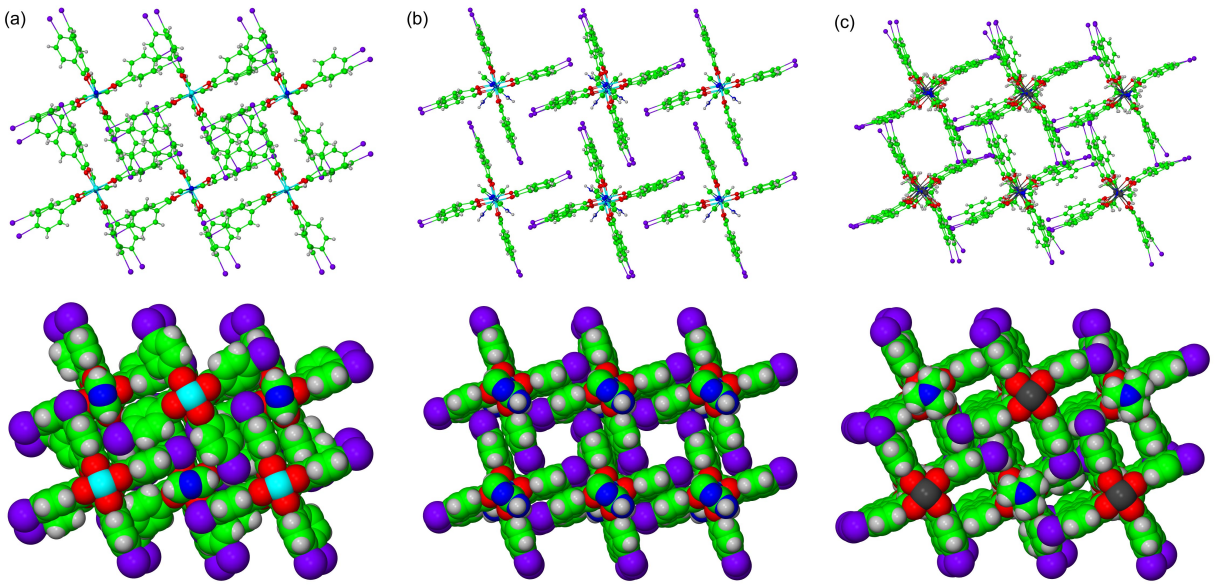

Fig. 5 Packing of the chains in the crystal structures of (a) $[Cu_2(ibz)_4(pyz)]$ **4**, (b) $[Cu_2(ibz)_4(apyz)]\cdot 2BzOH$ **5** and (c) $[Zn_2(ibz)_4(dabco)]\cdot 3.25DMF$ **6**. Included solvent molecules have been removed for clarity.

For **5**, the distance between neighbouring chains along both the *a* and *b* axes is 12.8 Å (Fig. 5b), significantly greater than that in **4**. As a consequence, there are channels present in **5** of approximate dimensions 3.9 × 3.7 Å. The greater distance between the chains with respect to that in **4** is related to supramolecular interactions involving the 4-iodobenzoate ligands. There is no interdigitation in **5**, but pairwise stacking of the 4-iodophenyl groups suggests the

presence of π···π interactions between these. The twists in the ligands between the carboxylate groups and phenyl rings are relatively small (8° - 20°).

For **6**, there are also channels within the structure, though these are puckered due to kinking of the chains (Fig. 5c). The distance between chains is less than in **5**, being 11.5 Å along the *b* and *c* axes, and as a consequence the channels are narrower (approximate dimensions 4.9 × 2.9 Å). In **6** there are C–H···I interactions involving the 4-iodobenzoate ligands on neighbouring chains. The twists in the ligands between the carboxylate groups and phenyl tings are relatively small and similar to those in **5** (7° - 21°). There is evidence of halogen bonding[23] between the iodine atoms on some of the 4-iodobenzoate ligands and the oxygen atoms of the included DMF molecules [I···O 2.981 - 3.227 Å, C–I···O 158-168°]. These contacts pull the 4-iodobenzoate group away from the paddle wheels, and lead to distortions from linearity in the chains.

The channels in **5** and **6** house included solvent molecules, though in both cases removal of the solvent under a range of conditions led to loss of crystallinity, as with **1-3**.

*Structures of the 4,4'-bipyridine-linked coordination polymers $[Cu(bpc)_2(4,4'\text{-bipy})(BzOH)_2]\cdot 2BzOH$ **7**, $[Zn(bpc)_2(4,4'\text{-bipy})]$ **8** and $[Zn(ibz)_2(4,4'\text{-bipy})]$ **9***

The asymmetric unit for compound **7** consists of half a copper atom, one bpc ligand, half a 4,4'-bipy ligand and two benzyl alcohol molecules. The copper atoms exhibit Jahn-Teller distorted octahedral geometry, coordinating to two 4,4'-bipy ligands and to two monodentate bpc ligands in the equatorial plane [Cu(1)–N(1) 1.9986(19), Cu(1)–N(2) 2.0222(18) Å, Cu(1)–O(1) 1.9609(11) Å] and to two benzyl alcohol ligands in the axial positions [Cu(1)–O(3) 2.538(2) Å]. Coordination of the BzOH ligands is reinforced by hydrogen bonding of the hydroxyl groups to the uncoordinated oxygen atoms of the bpc carboxylate groups [O(3)···O(2) 2.696 Å, H(3A)···O(2) 1.89 Å, O(3)–H(3A)···O(2) 161°].

The 4,4'-bipy ligands link the copper centres into linear one-dimensional chains as shown in Fig. 6, which pack into sheets with the bpc ligands in one chain projecting into the gaps between bpc ligands in the neighbouring chain. This leads to efficient packing with no significant voids or channels. The bpc ligands are twisted, with an angle of 19° between the

carboxylate mean plane and that of the attached phenyl ring, and an angle of 26° between the two phenyl ring mean planes.

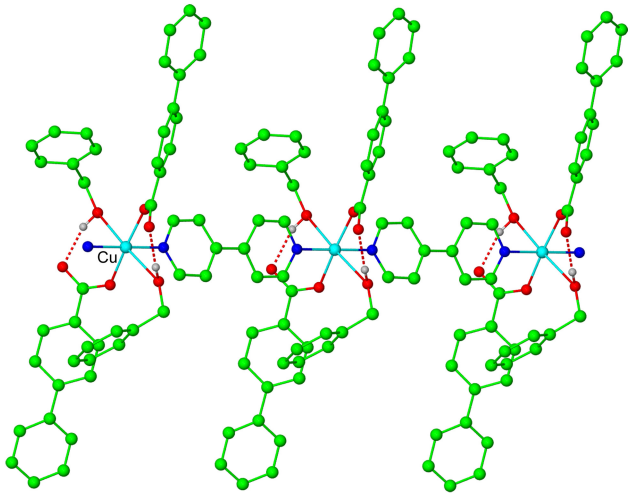

Fig. 6 The crystal structure of $[Cu(bpc)_2(4,4'\text{-bipy})(BzOH)_2]\cdot 2BzOH$ **7**, showing the linear one-dimensional chains.

The asymmetric unit for compound **8** contains two zinc metal centres, four bpc ligands and two 4,4'-bipy linkers. Each zinc centre is coordinated to two bpc ligands and to two 4,4'-bipy ligands. The bridging nature of the latter extends the structure into one-dimensional chains (Fig. 7). There is a difference in the coordination environment of the two independent zinc centres, as Zn(1) exhibits distorted octahedral geometry, with the two carboxylate groups bidentate [Zn(1)–O 2.069(6) – 2.426(5) Å], whereas Zn(2) has distorted tetrahedral geometry, with the two carboxylate groups monodentate [Zn(2)–O(5) 1.923(3) Å, Zn(2)–O(7) 1.936(3) Å].

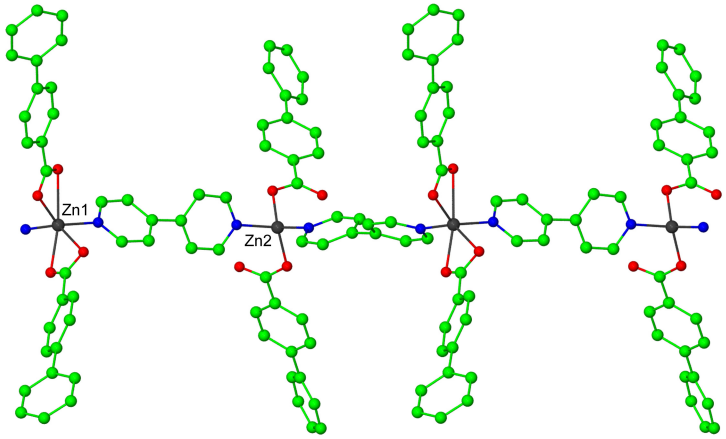

Fig. 7 The crystal structure of [Zn(bpc)$_2$(4,4'-bipy)] **8**, showing the zigzag one-dimensional chains.

Despite the differences in metal geometry, the N–Zn–N angles are similar [N(1)–Zn(1)–N(3) 100.91(17)°, N(2)–Zn(2)–N(4) 101.68(17)°], and the chains are zigzagged, running parallel to each other. Neighbouring chains embrace, supported by C–H···O interactions, and there are no significant pores of channels within the structure.

The asymmetric unit for **9** consists of one zinc centre, two 4-iodobenzoate ligands and one 4,4'-bipy ligand. The zinc centres exhibit approximately tetrahedral geometry with the two 4-iodobenzoate ligands coordinating in a monodentate manner [Zn(1)–O(1) 2.007(6) Å, Zn(1)–O(3) 1.942(5) Å]. The other two positions of the zinc coordination sphere are occupied by two nitrogen atoms from the bipy ligands [Zn(1)–N(1) 2.067(6) Å, Zn(1)–N(2) 2.062(5) Å] which link adjacent zinc atoms together. Due to the tetrahedral geometry of the metal centres, the structure forms one-dimensional zigzag chains (Fig. 8), similar to those observed in **8**. In contrast to **8**, however, the chains in **9** do not all run in the same direction, but pack as interpenetrated sheets at 95° to each other. At the positions where the chains from these sheets cross there are π···π interactions between the phenyl rings from the 4,4'-bipy ligands. There are no significant voids or channels in the structure.

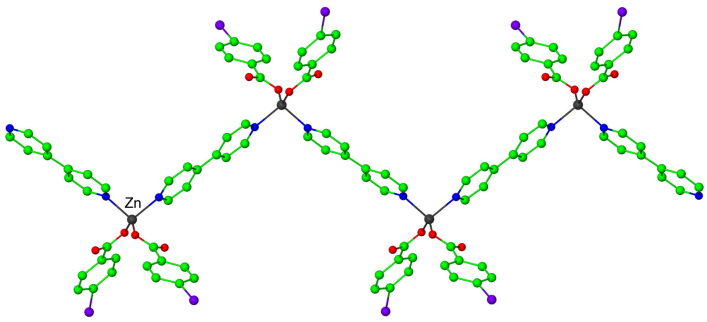

Fig. 8 The crystal structure of [Zn(ibz)$_2$(4,4'-bipy)] **9**, showing the zigzag one-dimensional chains.

Discussion

Compounds **1-6** all form the anticipated structures in which coordination polymers based on the linking of $M_2(O_2CR)_4$ paddle wheel units run parallel to each other. In five of the six

structures, the packing of the chains leads to formation of solvent-filled channels within the structure. Only in **4** does significant interdigitation occur to bring the chains closer together and allow them to pack without accessible channels being formed. The offsetting of neighbouring chains with respect to each other allows them to pack more efficiently, thus reducing the size of the channels. Hence, **2** and **3**, with all neighbouring chains offset from each other pack more efficiently than **1**, in which both offset and non-offset neighbours are present (Fig. 9). In a similar manner, **4** with only offset chains packs more efficiently than either **5** or **6**, which both have neighbouring chains that are not offset.

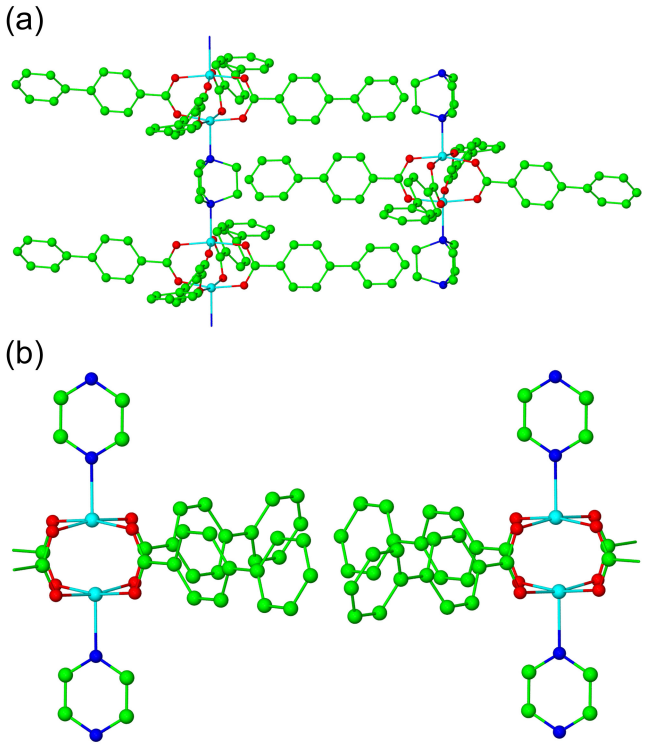

Fig. 9 Examples of (a) offset and (b) non-offset neighbouring chains. Offsetting allows the chains to pack closer together.

In contrast to **1-6**, compounds **7-9** form structures in which single metal centres are bridged by 4,4'-bipy ligands into chains. There are many examples of paddle wheel dimers bridged by 4,4'-bipy into infinite chains, so the type of structure observed in **1-6** is clearly feasible. For example, the compound $[Cu_2(O_2CPh)_4(4,4'\text{-bipy})]$[24] forms one-dimensional chains similar to those in **1-6**, though in contrast to these structures the chains do not all run in the same direction, and consequently channels are absent from the structure. The larger 'windows' present with neighbouring 4,4'-bipy-based chains may facilitate formation of structures with

chains running in different directions, as it is easier for chains to thread through these larger windows.

Despite the presence of channels in the crystal structures of **1-3** and **5-6**, the compounds all lose crystallinity on removal of the solvent from the channels and, as yet, it has not been possible to characterise an 'empty pore' framework for bpc. While it is possible that loss of crystallinity could be avoided by the use of very mild activation (*e.g.* supercritical CO_2[25] or freeze drying[26]), the loss of crystallinity on removal of the guests from the pores may be indicative of flexibility, with the chains able to move with respect to each other once the channels are empty.[27] This is consistent with previous observations on $[Cu_2(O_2CPh)_4(pyz)]$, for which CO_2 adsorption occurs with expansion of the channels via a combination of an extension of interchain distances, tilt of $\pi\cdots\pi$ stacked rings and a slide in the neighbouring chains with respect to each other.[18] Similar observations were observed with inclusion of alcohols[28] and acetone,[29] with the latter leading to an increase in the cell volume of 14%, which is linked to expansions in the interchain distances along the *c*- and *a*-axes from 9.5 to 10.8 Å, and 8.7 to 8.9 Å respectively. Current work is concentrated on improving the synthesis of these materials and ascertaining whether similar flexibility exists in these larger channel structures.

Conclusions

Nine new copper and zinc coordination polymers using the biphenyl-4-carboxylate (bpc) or 4-iodobenzoate (ibz) ligands together with a ditopic nitrogen donor linker have been synthesised and crystallographically characterised. Compounds **1-6** contain the metal paddle wheel SBUs, and these dimers are linked into one-dimensional chains through the use of pyrazine, 2-aminopyrazine or dabco as bridging ligands. The chains pack in a similar manner to those in $[Cu_2(O_2CPh)_4(pyz)]$, with the majority having larger channels than those reported for this compound due to the longer substituents on the carboxylates. This demonstrates that the envisaged poorer packing engendered by using longer ligands is an attractive strategy to preparing materials with larger channels. On increasing the length of the nitrogen donor linker to bipy, different structural types are formed. Compounds **7-9** all contain one-dimensional chains, but these contain linked single metal centres as opposed to dimers. The chains in these compounds pack in such a way that channels are not created. Longer *N,N′*-

ditopic ligands therefore disfavour the desired parallel chains architecture, with the increased ligand length allowing for the formation of other structural types.

Experimental

General points

All reagents used for the synthesis of compounds **1-9** were obtained commercially and used without further purification. Powder X-ray diffraction measurements were recorded using a Bruker D8 powder diffractometer, fitted with Goebel mirrors, and using CuK_{α} radiation of wavelength 1.5414 Å. Samples were placed in 0.3, 0.5 or 0.7 mm diameter Lindemann capillaries, and measured with a 2θ range of 4 - 60°. The step size was 0.02° with time per step of 1.00s. Elemental analyses were conducted by Alan Carver (University of Bath). Thermogravimetric analyses were recorded on a Perkin Elmer TGA 4000 Thermogravimetric analyzer, with a temperature range of 40-600 °C at 5 °C per minute under an atmosphere of nitrogen.

*Synthesis of $[Cu_2(bpc)_4(pyz)]\cdot 3.8BzOH$, **1***

Hbpc (0.099 g, 0.50 mmol) and pyrazine (pyz) (0.041 g, 0.50 mmol) were dissolved in benzyl alcohol (6 cm^3) with gentle heating and stirring. Once cooled, benzyl alcohol (2 cm^3) was gently layered on top of this solution. Layered on top of this was a solution of $Cu(OAc)_2\cdot H_2O$ (0.037 g, 0.19 mmol) dissolved in methanol (6 cm^3). The vial was sealed, and the solution left undisturbed for several days to yield crystals of suitable size for single crystal X-ray diffraction. Yield 0.0564 g. The X-ray powder diffraction trace (Fig. S1) and elemental analysis showed evidence for the bulk sample being phase impure, and despite variations in the reaction conditions a pure bulk sample of **1** was not obtained. Another possibility is that a transformation takes place on grinding.

*Synthesis of $[Cu_2(bpc)_4(dabco)]\cdot BzOH$, **2***

Hbpc (0.099 g, 0.50 mmol) and dabco (0.056 g, 0.50 mmol) were dissolved in benzyl alcohol (BzOH) (6 cm^3) with gentle heating and stirring. Once cooled, benzyl alcohol (2 cm^3) was gently layered on top of this solution. Layered on top of this was a solution of $Cu(OAc)_2\cdot H_2O$ (0.038 g, 0.19 mmol) dissolved in methanol (6 cm^3). The vial was sealed, and the solution left for several days to yield crystals of suitable size for single crystal X-ray diffraction. Yield

0.0818 g. Found: C, 65.7; H, 5.17; N, 2.52. $C_{58}H_{48}Cu_2N_2O_8$ requires C, 67.7; H, 4.71; N, 2.73%. The X-ray powder diffraction pattern (Fig. S2) showed the sample to be impure, with an unidentified by-product present; this result is in line with the elemental analysis. The TGA (Fig. S3) shows a percentage mass loss of approximately 9.5 % at 170 °C which can be attributed to the loss of the guest benzyl alcohol molecule (calc. 9.5 %). However, there is no clear plateau in the TGA trace, suggesting solvent loss occurs alongside decomposition.

Synthesis of $[Zn_2(bpc)_4(dabco)]\cdot 2DMF$, ***3***

Hbpc (0.334 g, 1.68mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.250 g, 0.84 mmol) and dabco (0.093 g, 0.83 mmol) were dissolved in DMF (10 cm^3), and placed in a 20 cm^3 pressure tube. The tube was sealed and heated to 120°C for 2 days. Once cooled to room temperature, crystals of suitable size for single crystal X-ray diffraction were obtained after several days. Yield 0.334 g (63 %). Found: C, 64.8; H, 5.25; N, 4.68. $C_{64}H_{62}N_4O_{10}Zn_2$ requires C, 65.2; H, 5.31; N, 4.76%. The X-ray powder diffraction pattern of **3** confirmed the sample was phase pure (Fig. S4). The TGA (Fig. S5) shows a percentage mass loss of approximately 13 % up to 170 °C which can be attributed to the release of the included DMF molecules from the pores (calc. 12.4 %).

Synthesis of $[Cu_2(ibz)_4(pyz)]$, ***4***

Hibz (0.124 g, 0.50 mmol) and pyrazine (0.041 g, 0.50 mmol) were dissolved in benzyl alcohol (6 cm^3) with gently heating and stirring. Once cooled, benzyl alcohol (2 cm^3) was gently layered on top of this solution. Layered on top of this was a solution of $Cu(OAc)_2\cdot H_2O$ (0.038 g, 0.19 mmol) dissolved in methanol (6 cm^3). The vial was sealed, and the solution left for several days after which crystals of suitable size for single crystal X-ray diffraction were obtained. Yield 0.0794 g (70 %). Found: C, 32.5; H, 1.81; N, 2.46. $C_{32}H_{20}Cu_2N_2O_8I_4$ requires C, 32.1; H, 1.69; N, 2.34%. The X-ray powder diffraction pattern confirmed that **4** was the only product present (Fig. S6). The TGA exhibits only a decomposition of the complex at around 250 °C, confirming no solvent to be present in the pores (Fig. S7).

Synthesis of $[Cu_2(ibz)_4(apyz)]\cdot 2BzOH$, ***5***

Hibz (0.125 g, 0.50 mmol) and 2-aminopyrazine (0.049 g, 0.51 mmol) were dissolved in benzyl alcohol (6 cm^3) with gentle heating and stirring. Once cooled, benzyl alcohol (2 cm^3) was gently layered on top of this solution. Layered on top of this was a solution of $Cu(OAc)_2\cdot H_2O$ (0.038 g, 0.19 mmol) dissolved in methanol (6 cm^3). The vial was sealed, and the solution left for several days after which crystals of suitable size for single crystal X-ray

diffraction were obtained. Yield 0.0971 g (72 %). The X-ray powder diffraction pattern of **5** showed a good match to the pattern simulated from the crystal data (Fig. S8) though satisfactory microanalysis could not be otained. The TGA for **5** showed a weight loss of approximately 23 % up to 140 °C, this can be attributed to the loss of three molecules of benzyl alcohol (Fig. S9). This is more than expected from the crystal structure, though in this the solvent molecules were diffuse, hence the quantity was estimated.

Synthesis of $[Zn_2(ibz)_4(dabco)]\cdot 3.25DMF$, ***6***

Hibz (0.422 g, 1.70 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.248 g, 0.84 mmol) and dabco (0.092 g, 0.82 mmol) were dissolved in DMF (10 cm^3), and placed in a 20 cm^3 pressure tube. The tube was sealed and heated to 120°C for 2 days. . Once cooled to room temperature, crystals of suitable size for single crystal X-ray diffraction were obtained after several days. Yield 0.1999 g. Found: C, 36.0; H, 3.12; N, 4.46. $C_{43}H_{49}I_4N_5O_{11}Zn_2$ requires C, 35.6; H, 3.41; N, 4.83%. The X-ray powder diffraction pattern for **6** shows there to be a poor match with those calculated from the crystal data, with an unidentified material also present (Fig. S10). The TGA shows a percentage weight loss of approximately 20 % up to 300 °C (Fig. S11) which can be attributed to the release of DMF from the pores (calc. 16.2%). However, there is no clear plateau in the TGA trace, suggesting solvent loss occurs alongside decomposition.

Synthesis of $[Cu(bpc)_2(4,4'\text{-bipy})]\cdot 4BzOH$, 7

Hbpc (0.099 g, 0.50 mmol) and 4,4'-bipyridyl (0.078 g, 0.50 mmol) were dissolved in benzyl alcohol (6 cm^3) with gentle heating and stirring. Once cooled, benzyl alcohol (2 cm^3) was gently layered on top of this solution. Layered on top of this was a solution of $Cu(OAc)_2\cdot H_2O$ (0.050 g, 0.25 mmol) dissolved in methanol (6 cm^3). The vial was sealed, and the solution left undisturbed for several days to yield crystals of suitable size for single crystal X-ray diffraction. The reaction produced blue crystals of **7**, and a green unidentified product. The blue crystals were separated manually from this mixture for analysis, and the X-ray powder diffraction confirmed that **7** was the major product (Fig. S12). Found: C, 73.1; H, 5.50; N, 2.71. $C_{64}H_{58}CuN_2O_8$ requires C, 73.4; H, 5.59; N, 2.68%.

Synthesis of $[Zn_2(bpc)_4(bipy)_2]$, ***8***

Hbpc (0.327 g, 1.65mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.252 g, 0.85 mmol) and bipy (0.063 g, 0.40 mmol) were dissolved in DMF (10 cm^3), and placed in a 20 cm^3 pressure tube. The tube was sealed and heated to 120°C for 2 days. Once cooled to room temperature, crystals of suitable

size for single crystal X-ray diffraction were obtained after several days. Yield 0.1949 g (79 %). Found: C, 64.8; H, 5.25; N, 4.68. $C_{64}H_{62}N_4O_{10}Zn_2$ requires C, 65.2; H, 5.31; N,4.76%. The X-ray powder diffraction pattern confirmed that the bulk material is compound **8** (Fig. S13).

Synthesis of [Zn(ibz)$_2$(4,4'-bipy)], ***9***

Hibz (0.416 g, 1.68mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.248 g, 0.84 mmol) and 4,4'-bipyridyl (0.144 g, 0.92 mmol) were dissolved in DMF (10 cm^3), and placed in a 20 cm^3 pressure tube. The tube was sealed and heated to 120°C for 2 days. Once cooled to room temperature, crystals of suitable size for single crystal X-ray diffraction were obtained after several days. Yield 0.3067 g (51 %). Found: C, 40.1; H, 2.28; N, 4.01. $C_{48}H_{32}N_4O_8Zn_2I_4$ requires C, 40.3; H, 52.25; N, 3.92%. The X-ray powder diffraction for compound **9** was carried out and confirms the phase purity of this material (Fig. S14).

Crystallography

X-ray data for compounds **1**, **5** and **7-9** were collected on a Nonius Kappa CCD diffractometer using Mo-K_α radiation, while those for compound **2** were measured on a Bruker APEX II diffractometer using synchrotron radiation (λ = 0.69450 Å) at Station 9.8 of the SRS Daresbury Laboratory. A Bruker Apex II diffractometer using synchrotron radiation (λ = 0.7749 Å) at Station 11.3.1 of the ALS Lawrence Berkeley National Laboratory was used to collect the single crystal data for compounds **3** and **6**. X-ray data for compound **4** was collected on an Oxford Diffraction Gemini diffractometer fitted with an Atlas CCD detector, using Mo-K_α radiation. Unless noted, all non-hydrogen atoms were refined anisotropically in the final least squares run, and hydrogen atoms were included at calculated positions. The structures were solved using SHELXS-97 and refined using full-matrix least squares in SHELXL-97.

Refinements were generally straightforward with the following exceptions and points of note. For **1**, the oxygen of the benzyl alcohol solvent moiety was disordered equally over two proximate sites. The associated hydrogens could not be reliably located so were omitted from the final refinement. Compound **3** contained a solvent DMF molecule which was disordered over two sites (55:45). The dabco CH_2 groups were equally disordered due to the nitrogen atoms being located on a crystallographic 2-fold rotation axis. Due to the poor diffracting ability of the crystal at higher Bragg angles, the data was truncated at 20°. The

crystallographic data for **5** were poor, as the intensity of the reflections dropped off above Bragg angles of 14°. Nonetheless, an unambiguous structural model was still obtained. The asymmetric unit for compound **6** contained six full occupancy DMF molecules, and an additional half molecule of DMF located on an inversion centre. Some distance restraints were applied to the solvent molecules, and atomic displacement parameter restraints were applied to the dabco carbon atoms. All fragments with less than 50 % occupancy were treated isotropically. Large atomic displacement parameters were observed for the chelating carboxylate groups attached to Zn(1) in **8**. There is also residual electron density positioned here in the Fourier map. This indicates some disorder, however attempts to refine a sensible model where the carboxylate is disordered between monodentate and bidentate coordination were unsuccessful.

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Table 1. Crystal data and structure refinement for compounds **1-9**

Compound reference	**1**	**2**	**3**	**4**	**5**
Chemical formula	$C_{65.6}H_{61.5}Cu_2N_2O_{10.8}$	$C_{32.5}H_{29}CuNO_{4.5}$	$C_{64}H_{62}N_4O_{10}Zn_2$	$C_{16}H_{10}CuI_2NO_4$	$C_{46}H_{38}Cu_2I_4N_3O_{10}$
Formula Mass	1177.75	569.11	1177.92	597.59	1427.47
Crystal system	Triclinic	Monoclinic	Monoclinic	Tetragonal	Tetragonal
a/Å	9.7080(4)	23.320(3)	23.043(10)	18.7750(10)	12.7970(5)
b/Å	14.1110(9)	9.5701(14)	9.582(4)	18.7750(10)	12.7970(5)
c/Å	16.5790(10)	26.478(4)	26.852(11)	19.672(3)	39.0980(18)
α/°	72.751(2)	90.00	90.00	90.00	90.00
β/°	87.723(4)	103.799(2)	104.624(7)	90.00	90.00
γ/°	71.095(3)	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	2048.0(2)	5738.7(14)	5737(4)	6934.4(10)	6402.8(5)
Temperature/K	150(2)	150(2)	100(2)	150(2)	150(2)
Space group	$P\bar{1}$	*C*2/*c*	*C*2/*c*	*I*41/*a*	*P*41
No. of formula units per unit cell, *Z*	1	8	4	16	4
Absorption coefficient, μ/mm^{-1}	0.564	0.800	0.899	4.841	2.637
No. of reflections measured	25559	22246	10340	12737	6739
No. of independent reflections	7222	5395	2253	5843	3262
R_{int}	0.0758	0.0727	0.1063	0.0284	0.1262
Final R_1 values ($I > 2\sigma(I)$)	0.0751	0.0768	0.0423	0.0668	0.0786
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1955	0.2140	0.0781	0.1750	0.2418
Final R_1 values (all data)	0.1103	0.1143	0.0804	0.1125	0.1056
Final $wR(F^2)$ values (all data)	0.2095	0.2340	0.0866	0.1890	0.2617
Goodness of fit on F^2	1.028	1.039	1.032	1.060	1.078
Flack parameter	-		-	-	0.45(9)

Compound reference	**6**	**7**	**8**	**9**
Chemical formula	$C_{87.5}H_{101.5}I_8N_{10.5}O_{22.5}Zn_4$	$C_{64}H_{58}CuN_2O_8$	$C_{72}H_{52}N_4O_8Zn_2$	$C_{24}H_{16}I_2N_2O_4Zn$
Formula Mass	2936.97	1046.66	1231.92	715.56
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	12.4072(8)	15.6030(2)	25.7330(6)	26.7860(7)
b/Å	12.4082(7)	11.1260(1)	13.5820(3)	24.7060(7)
c/Å	33.608(2)	29.8590(3)	17.2990(4)	7.4370(2)
α/°	87.891(2)	90.00	90.00	90.00
β/°	88.473(2)	90.711(1)	106.939(1)	104.858(2)
γ/°	83.785(2)	90.00	90.00	90.00
Unit cell volume/Å^3	5138.8(5)	5183.09(10)	5783.8(2)	4757.1(2)
Temperature/K	150(2)	150(2)	150(2)	150(2)
Space group	$P\bar{1}$	*C*2/*c*	*C*2	*C*2/*c*
No. of formula units per unit cell, *Z*	2	4	4	8
Absorption coefficient, μ/mm^{-1}	3.397	0.482	0.893	3.662
No. of reflections measured	52084	32492	51278	35694
No. of independent reflections	26906	5831	13211	5451
R_{int}	0.0604	0.0568	0.0980	0.0887
Final R_1 values ($I > 2\sigma(I)$)	0.0764	0.0391	0.0561	0.0591
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1937	0.0837	0.1289	0.1590
Final R_1 values (all data)	0.1137	0.0532	0.1073	0.0965
Final $wR(F^2)$ values (all data)	0.2210	0.0906	0.1506	0.1728
Goodness of fit on F^2	1.021	1.040	1.022	1.080
Flack parameter	-	-	-0.011(12)	-

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